

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Purifying Acrylonitrile by Distillation

5 We, AMERICAN CYANAMID COMPANY, a Corporation organised under the laws of the State of Maine, United States of America, of 30, Rockefeller Plaza, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the purifying of acrylonitrile. More particularly, it relates to refining crude acrylonitrile prepared by reacting acetylene with hydrocyanic acid in the presence of a catalyst.

15 In the past few years, commercial interest in acrylonitrile has expanded to the point where it has become one of the most important and promising organic chemical intermediates available. It is a particularly desirable intermediate in the manufacture of a wide range of products, for example, plastics, rubber, synthetic fibers, soil conditioners and the like. For many uses, acrylonitrile must be highly pure, and for this reason strict specifications of purity must be met in the commercial manufacture of acrylonitrile.

20 In the purification of crude acrylonitrile, it is the usual practice to recover the acrylonitrile content of the reactor gas, produced by reacting acetylene with hydrocyanic acid, by absorbing it in water. The resultant dilute acrylonitrile solution contains, in addition, various impurities, among which may be mentioned hydrogen cyanide, acetaldehyde and lactonitrile. Generally, the dilute aqueous solution is then steam stripped to obtain the acrylonitrile in a more concentrated form. This is then subjected to various refining steps whereby the acrylonitrile content is separated from the impurities.

25 The presence of both hydrogen cyanide and acetaldehyde constitutes a serious refining problem. Commercial standards with respect to the presence of both these impurities in acrylonitrile are extremely rigid. For instance,

commercial specifications state that no more than 5 ppm. hydrogen cyanide can be present in the final acrylonitrile product. The refining problem, moreover, is aggravated by the fact that lactonitrile becomes less stable at elevated temperatures and tends to dissociate into hydrogen cyanide and acetaldehyde.

30 A large proportion of the hydrogen cyanide and acetaldehyde content can be separated as lactonitrile in the still bottoms from the above-described steam stripping. However, at the high stripping temperatures employed, lactonitrile dissociates to some extent to hydrogen cyanide and acetaldehyde. These low boiling products are stripped overhead with the acrylonitrile. The overheads may then be further treated by various physical and/or chemical purification steps designed to reduce the hydrogen cyanide and acetaldehyde contents by removing them as such or in the form of lactonitrile.

35 A serious disadvantage of removing much of the hydrogen cyanide and acetaldehyde as lactonitrile in the aqueous bottoms from steam stripping is that these bottoms are eventually discharged in commercial practice with the plant effluent. This creates a disposal problem, since lactonitrile is extremely toxic. Accordingly, the plant effluent must be subjected to a far more severe predisposal treatment prior to discharge than would otherwise be practised. Additionally, such disposal represents an excessive loss of hydrogen cyanide.

40 There has remained, therefore, a demand for a purification procedure for crude acrylonitrile whereby hydrogen cyanide and acetaldehyde may be removed to within specification limits without, at the same time, contaminating the steam stripping effluent with lactonitrile and/or hydrogen cyanide. It is the primary object of this invention to fulfill this demand.

45 In the acrylonitrile solution, at room temperature, the system:—

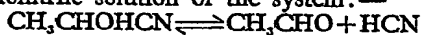
$$\text{CH}_3\text{CHO} + \text{HCN} \rightleftharpoons \text{CH}_3\text{CH}(\text{OH})\text{CN}$$
is at equilibrium far on the lactonitrile side.

[Price

At elevated temperatures, i.e., 100° C., dissociation to hydrogen cyanide and acetaldehyde is considerably greater. This system, moreover, approaches equilibrium much more rapidly in an aqueous acrylonitrile solution under substantially neutral to alkaline conditions than under acid conditions. The process of this invention takes advantage of this rate factor and thereby meets the objects of this invention in an unusually effective, yet surprisingly simple, manner.

In general, the process of this invention can be quite simply stated. The solution of acrylonitrile in water obtained from scrubbing the reactor gas is adjusted to an optimum hydrogen ion concentration for steam stripping. At the steam stripping temperature, the lactonitrile content partially dissociates to acetaldehyde and hydrogen cyanide. These, being low boiling compounds, are stripped overhead with the acrylonitrile. At the adjusted hydrogen ion concentration, the system continues to rapidly approach the equilibrium upset by stripping of acetaldehyde and hydrogen cyanide, so that within the time required to completely strip the acrylonitrile content from any given unit of feed to the stripper, the hydrogen cyanide and acetaldehyde formed by dissociation of the lactonitrile content, as well as any free hydrogen cyanide and acetaldehyde, can likewise be substantially completely stripped. The stripped impurities may then be separated from the acrylonitrile by means which form no part of this invention.

The solution of acrylonitrile in water obtained by scrubbing the reactor gas is acidic, the pH being above 3. In accordance with the process of this invention, the hydrogen ion concentration of the solution must be adjusted. It has been found that the rate at which equilibrium is approached in an aqueous acrylonitrile solution of the system:—



is sufficiently fast for the purpose of this invention at a pH higher than about 6. Adjustment of the hydrogen ion concentration of the solution generally will not be beyond a pH of about 9 and preferably will be from about 6.5 to 8.

Adjustment of the pH may be readily made by the addition of any of various alkaline materials, such as the hydroxides, phosphates, borates and carbonates of the alkali and alkaline earth metals, and ammonia. Addition of the alkaline material may be conveniently made at any of various stages prior to stripping. Preferably, addition is made at the time of scrubbing of the reactor gas, but the alkaline material may also be directly added to the stripping column, or at any point between the scrubber and the stripping column.

On condensation, the stripped overheads stratify into a lower water layer containing some acrylonitrile and an upper acrylonitrile layer containing some water in addition to

various other impurities including lactonitrile, acetaldehyde and hydrogen cyanide. The water layer may be returned as reflux to the stripping column and the acrylonitrile layer further treated in a manner which forms no part of this invention to obtain a purified acrylonitrile product.

The process of this invention is further explained by the following examples, which are intended to be illustrative only and not only by way of limitation. All parts are by weight unless otherwise indicated.

EXAMPLE 1

An aqueous acrylonitrile solution obtained by scrubbing with water a gas from the reaction of hydrogen cyanide with acetylene and having a total hydrogen cyanide concentration of 2140 ppm. of which 1140 ppm. is as free hydrogen cyanide and the remainder is in the form of lactonitrile, is adjusted to a pH of 6.3 by the addition of a 0.5N sodium hydroxide solution. The adjusted solution is stripped with steam over a period of 20 minutes at 100° C. After stripping, the concentration of hydrogen cyanide in the column bottoms, either in the form of lactonitrile or as free hydrogen cyanide, is found to be only 78 ppm.

EXAMPLE 2

An aqueous acrylonitrile solution similar to that of Example 1 but having a total hydrogen cyanide concentration of 2520 ppm. of which 1560 ppm. is as free hydrogen cyanide and the remainder is in the form of lactonitrile, is adjusted to a pH of 7.0. After stripping with steam for 20 minutes, the hydrogen cyanide concentration in the column bottoms, either in the form of hydrogen cyanide or in the form of lactonitrile, is found to be 77 ppm.

EXAMPLE 3

An aqueous acrylonitrile solution similar to that of Example 1 but having a total hydrogen cyanide concentration of about 5000 ppm., of which 3550 ppm. is as free hydrogen cyanide and the remainder is in the form of lactonitrile, is continuously neutralized to a pH of 6.0—8.0 by addition of caustic soda and then continuously stripped in a distillation column operated at essentially atmospheric pressure. The water effluent from the bottom of the column is found to contain only 10 ppm. hydrogen cyanide either in the form of lactonitrile or as free hydrogen cyanide.

EXAMPLE 4

To show the effect of improper pH adjustment Example 2 is repeated except that the hydrogen ion concentration is adjusted to a pH of 4.9. After stripping, the hydrogen cyanide concentration in the column bottoms, either as free hydrogen cyanide or as lactonitrile, is found to be 546 parts.

WHAT WE CLAIM IS:—

1. A process of refining crude acrylonitrile which comprises subjecting to stripping with steam a dilute aqueous solution comprising acrylonitrile, acetaldehyde, hydrogen cyanide and lactonitrile whereby acrylonitrile is stripped and recovered as a concentrated solution, the hydrogen ion concentration of the solution being maintained during stripping at a pH range of from 6 to 9 at which pH substantially all lactonitrile is dissociated and stripped overhead as acetaldehyde and hydrogen cyanide with the acrylonitrile and a sub-

stantially lactonitrile-free residue is obtained.

2. A process according to Claim 1, in which the pH is maintained in the desired range by addition of an hydroxide, phosphate, borate or carbonate of an alkali or alkaline earth metal or a corresponding ammonium compound. 15

3. A process of refining crude acrylonitrile substantially as hereinbefore described with reference to the examples. 20

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